ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

DETERMINATION OF A LOW-COST AGENT FOR SULFATE REMOVAL IN ANODIC OXIDATION PROCESS

M.Sc. THESIS

Ecem Müge ANDOĞLU

Department of Chemical Engineering

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ELOKSAL İŞLEM YAPAN FABRİKALARDA DÜŞÜK MALİYETLİ KİMYASAL KULLANIMI İLE SÜLFAT GİDERİMİ

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MAYIS 2015

Ecem Müge Andoğlu, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 506121008, successfully defended the **thesis** entitled "**DETERMINATION OF A LOW-COST AGENT FOR SULFATE REMOVAL IN ANODIC OXIDATION PROCESS**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To devoted researchers,

FOREWORD

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ABBREVIATIONS

AMD	**:** Acid Mining Drainage
COD	**:** Chemical Oxygen Demand
DI-60	**:** Pulp and paper waste
FAZ	**:** Synthesized Zeolite made from Fly Ash
FF	**:** Flotation Fines
FS	**:** Filter Sand
NF	**:** Nanofiltration
OIZ	**:** Organized Industrial Zone
RGC	**:** Wood-based activated carbon
PAC	**:** Polyaluminum salt
RH	**:** Iron sand
TFC	**:** Thin-Film Composite
UASB	**:** Up flow Anaerobic Sludge Blanket

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DETERMINATION OF A LOW-COST AGENT FOR SULFATE REMOVAL IN ANODIC OXIDATION PROCESS

SUMMARY

The surface treatment of and by metals dates back to early man using gold decoratively before 4000 BC. One of the surface treatment methods is anodic oxidation. Anodic oxidation, or anodizing, is an electrolytic process for producing very much thicker oxide coatings whose improved physical and chemical properties have greatly increased the field of application for aluminum. Sulfuric acid soon became and, remains the most common anodizing electrolyte.

In anodizing process, 18-20% concentration of sulfuric acid is used as the electrolyte. Due to sulfuric acid ionize to H^+ and SO_4^{2-}, anodizing wastewaters contain high sulfate concentration. High concentrations of sulfate in drinking water may cause transitory diarrhea. In Turkey, sulfate concentration limit is 250 mg/L in drinking water and 1700 mg/L for the industrial plants at the organized industrial zones (OIZ, industrial park).

This study aims to investigate sulfate removal from an acidic wastewater, which is obtained from an Aluminum Profile Production and Anodizing Plant located in Bilecik. The experiments were performed under the same conditions of the treatment facility of the factory. $BaCl_2.H_2O$, which is currently used in the treatment facility of factory, was applied with different amounts. $CaCl_2$ and KCl were selected as alternative chemicals to $BaCl_2.H_2O$ and were used with different amounts in the experimental trials. Besides, the effect of the flocculants and the basic effluent, which is used for neutralization, was also investigated.

As an important result of the study, it was determined that chemical costs of the treatment facility can be decreased by changing the chemical type and amounts.

In the first section; the aim, scope and the literature about the investigation of sulfate treatment methods were given.

In the second section; theoretical knowledge about anodic oxidation process and aluminum plant information were presented.

In the third section; the chemical precipitation by $BaCl_2.H_2O$, $CaCl_2$, KCl, and neutralization with basic effluent methodologies were explained.

In the fourth section; the results of experiments were given and they were comparatively assessed.

In the fifth section, the evaluation of experimental results was presented.

ELOKSAL İŞLEM YAPAN FABRKALARDA DÜŞÜK MALİYETLİ KİMYASAL KULLANIMI İLE SÜLFAT GİDERİMİ

ÖZET

Bu çalışmada alüminyum profil üretimi yapan ve eloksal prosesi kullanan bir alüminyum fabrikasının asidik atık suyundaki sülfatın kimyasal çöktürme yöntemi ile arıtılması konusu incelenmiştir.

Çalışmanın amacı, Bilecik 1. Organize Sanayi Bölgesi'nde bulunan bir alüminyum fabrikasının eloksal prosesi sonucu ortaya çıkan ve yaklaşık 7000 mg/L sülfat içeren atıksuyunun daha ekonomik ve çevreye daha az zararlı şekilde arıtılmasıdır. Fabrika halihazırda kullandığı kimyasal tipi ve miktarı ile atıksudaki sülfat miktarını yaklaşık 2000 mg/L'ye düşürebilmektedir. Uygulanan şekliyle yöntem hem fazla maliyet getirmekte, hem de istenilen arıtım sonuçlarına ulaşılamamaktadır. Bu çalışmada kullanılan kimyasal miktarının düşürülmesi ve kimyasal tipinin alternatif kimyasallarla değiştirilmesi ile maliyetlerin düşürülmesi ve çıkan atığın kirlilik yükünün azaltılması amaçlanmıştır.

Eloksal kelimesi Türkçe'ye Almanca "*el*ektrolytische *Ox*idation von *Al*uminium" kelimelerinin ilk iki harflerden oluşan kısaltmadan geçmiş olup, dünya literatüründe anodik oksidasyon (anodic oxidation) olarak bilinmektedir. Eloksal işlemi dekorasyon, mimari uygulamalar ve endüstriyel uygulamalar için istenen özellikte ürün elde edilen, alüminyum ürünlere uygulanan en önemli yüzey işlemlerden biridir. Eloksal sistemi çeşitli yöntemlerle külçeden elde edilen alüminyum profillerin bir dizi banyodan geçirilmesiyle gerçekleşen elektrokimyasal bir prosestir. Bu işlemde anot kaplanacak olan alüminyum iken, elektrolit asidik bir çözeltidir. Bu işlem genel olarak yağ alma, dağlama, nötralizasyon, anodizasyon, renklendirme ve tespit ile bunların durulama banyolarından oluşur. Anodizasyonda asidik çözelti olarak okzalik asit, kromik asit, fosforik asit veya sülfürik asit çözeltileri kullanlır ancak sülfürik asit en yaygın olanıdır. Sülfürik asit çözeltisi yüksek miktarda (%18-20) asit içermekte, işlem sırasında iyonlaşan sülfat yüksek konsantrasyonlara erişerek atıksudaki kirlilik yükünü arttırmaktadır.

İncelenen alüminyum fabrikası Bilecik ili 1. Organize Sanayi Bölgesi içerisinde yer almaktadır. Fabrikanın üretim prosesi temel olarak dökümhane, ekstrüzyon, yüzey işleme ve eloksal olmak üzere dört bölümden oluşmaktadır. Dökümhanede hurda alüminyum külçeleri ve katkı metalleri ile istenen alüminyum karışımından biyet elde edilmekte, ekstrüzyon işlemi ile profil şekline getirilmekte; yüzey işleme bölümünde müşteri isteklerine göre görünüş elde edilmesi sağlanmakta ve eloksal prosesi ile dayanımı arttırıldıktan sonra satışa sunulmaktadır. Bu işlemlerden biri asidik, diğeri bazik olmak üzere iki çeşit atıksu meydana gelmektedir. Yüksek konsantrasyonda sülfat içeren asidik atıksuya suda çözünmüş $BaCl_2.2H_2O$ eklenerek sülfat iyonlarının $BaSO_4$ tuzu olarak çökmesi

sağlanmakta, bazik atıksu ile de nötralizasyon işlemi gerçekleştirilmektedir. Arıtma çamurunun hızlı çöktürülmesi amacıyla karışıma flokülant eklenmektedir. Temizlenen suya kontrol analizler yapılmakta ve elde edilen değerler Atıksu Kontol Yönetmeliği'ne uygun ise ikinci bir arıtım için Organize Sanayi Bölgesi Atıksu Arıtma Tesisi'ne; arıtma çamuru ise çöktürme havuzlarının diplerinden preslerle alınarak OSB Katı Atık Sahası'na gönderilmektedir.

Tesisin eloksal bölümü 1 adet yağ alma, 3 adet dağlama, 2 adet nötralizasyon, 5 adet anodizasyon, kalay, nikel ve demir olmak üzere 3 adet renklendirme, 3 adet tespit, 1 adet son temizleme banyosu ve 14 adet durulama olmak üzere 32 adet banyodan oluşmaktadır. Anodizasyon ve nötralizasyon banyoları sülfürik asit kullanımından dolayı yüksek oranda asidik özelliğe sahipken; dağlama ve tespit banyoları sodyum hidroksit kullanımından dolayı yüksek miktarda bazik içeriğe sahiptir. Ayrıca metalik renklendirme banyoları da metal iyonları yanında sülfürik asit içerdiğinden asidik özellik taşımaktadır.

Bu çalışmada, tesiste uygulanan sistem laboratuvar ortamında oluşturulmuş; çöktürme kimyasalları olarak $BaCl_2.2H_2O$ ile birlikte, ekonomik ve çevresel yönden $BaCl_2.2H_2O$'e alternatif olabilecek olan $CaCl_2$ ve KCl kullanılmıştır. Deney sistemi olarak dörtlü karıştırıcılı jar test sistemi kullanılmıştır. Kimyasal miktarı olarak tesiste halihazırda kullanılmakta olan miktar referans alınmış, belli oranlarda azaltılarak denemeler yapılmıştır. Ayrıca belirli bir miktar sabit tutularak üç farklı kimyasal ile arıtılan su üzerine farklı miktarlarda flokülant eklenerek flokülantın sülfat giderimine etkisi araştırılmıştır. Bunların yanında bazik atıksuyun da karışık endüstiyel atıksu olması sebebiyle sülfat konsantrasyonuna etkisi tespit edilmek üzere çöktürücü kimyasal kullanılmadan da denemeler yapılmıştır. Denemeler sonunda elde edilen arıtılmış suyun sülfat miktarı standartlara uygun olarak spektrofotometre kullanılarak tespit edilmiştir.

Yapılan deneyler sonucunda, fabrika atıksuyundaki sülfat iyonlarının kullanılan kimyasal tipi ve miktarının değiştirilmesi ile daha ekonomik ve çevreye daha az zararlı bir şekilde giderilebileceği tespit edilmiştir. Ayrıca flokülant kullanımının farklı kimyasallar ile yapılan arıtımlara etkisinin değiştiği görülmüş, bazı kimyasalların kullanımında flokülanta ihtiyaç duyulmadığı anlaşılmıştır. Bunların yanında, bazik atıksuyun da sülfat giderimi üzerine etkisi olduğu anlaşılmış, kullanılan bazik atıksu miktarının arttırılmasıyla sudaki sülfat miktarının azaldığı görülmüştür.

Bu çalışmada, birinci bölümde yapılan çalışmanın amacı ve önemi ile endüstriyel atıksulardan sülfat giderimi ilgili bir literatür incelemesi verilmiştir.

İkinci bölümde eloksal prosesinin uygulanması ve reaksiyonları hakkında teorik bilgi verilmiştir. Alüminyum fabrikasının departmanları ile eloksal ve atıksu arıtım bölümleri hakkında bilgi verilmiştir.

Üçüncü bölümde deneysel metod verilerek $BaCl_2.H_2O$, $CaCl_2$, KCl kimyasallarının seçimi, bu kimyasallarla kimyasal çöktürme işlemi ve bazik atık su ile nötralizasyon işlemlerinin şartları ve adımları belirtilmiştir. Standartlara uygun olarak gerçekleştirilen sülfat analiz metodu açıklanmıştır.

Dördüncü bölümde fabrika atık suyunun arıtımında en uygun kimyasal tipi ve miktarının belirlenmesi amacıyla gerçekleştirilen deneylerin sonuçları verilmiş ve bunlar tartışılmıştır. Sonuç olarak kullanılan $BaCl_2.H_2O$, $CaCl_2$ ve KCl kimyasallarının ve kullanım miktarlarının sülfat giderimi üzerine etkilerinin

farklı olmasıyla beraber tüm sonuçlar yasal olarak belirtilen limiti sağlamıştır. Sonuçlar göz önüne alınarak yapılacak optimum kimyasal tipi ve miktarı seçimi ile işletmenin atıksu arıtma tesisi kimyasal madde giderlerinin ciddi ölçüde azaltılabileceği anlaşılmıştır.

Beşinci bölümde deneysel çalışma sonuçlarının değerlendirilmesi yapılmıştır.

1. INTRODUCTION

1.1 General Information

The surface treatment of and by metals dates back to early man using gold decoratively before 4000 BC. One of the surface treatment methods is anodic oxidation. Anodic oxidation, or anodizing, is an electrolytic process for producing very much thicker oxide coatings whose improved physical and chemical properties have greatly increased the field of application for aluminum. Aluminum is normally (90 % of cases) anodized in sulfuric acid electrolyte (Henley, 1982; EC, 2006).

Based on the use of sulfuric acid, anodizing wastewaters contain high sulfate concentration. High concentrations of sulfate in drinking water may cause transitory diarrhea (U.S. EPA, 1990). A study of adults found that most experienced a laxative effect above 1000 mg/L, whereas medical case reports indicate that bottle-fed infants develop diarrhea at sulfate levels above 600 mg/L (Cohn et al., 1999). In Turkey, sulfate concentration limit is 250 mg/L in drinking water and 1700 mg/L for the industrial plants at the organized industrial zones (OIZ, industrial park) (PHI, 2013; MEUP, 2014).

In this study, the effluent, which was obtained from an aluminum profile production and anodizing plant located at the first OIZ (Organized Industrial Zone) in Bilecik was used. The plant has several departments such as die workshop, extrusion press lines, surface treatment processes, anodizing plants, powder coating lines, decorative film coating unit, mechanical treatment unit, shrink unit, warehouse, quality control units and laboratories, wastewater treatment facility, casthouse and recycling plant.

Because of the sulfuric acid (18-20%) is used for the anodic oxidation process, the effluent contains high sulfate concentration. The concentration can be considered as 7000 mg/L in an average. Chemical precipitation method was performed for the removal of sulfate ions in the study. Three different chemicals were used with varied concentrations.

The determination of the most effective and the cheapest chemical agent for the separation of sulfate was the main goal of the study. The Plant decreases the high sulfate concentration (~7000 mg/L) to approximately 2000 mg/L by using certain amount of $BaCl_2.2H_2O$ and then sends this treated water to the wastewater treatment facility of OIZ. ~2000 mg/L sulfate is still a high concentration and it increases the OIZ shared treatment plant's pollution load. Besides, the Plant uses a costly method in an effort to reach this 2000 mg/L concentration, which is already high and thus the total economy of the facility is affected negatively. This situation is the same for the other Aluminum Anodizing Plants as well.

In this study, the possibilities of obtaining a cheaper and more effective sulfate removal agent were investigated. Achieving this goal would bring a significant contribution to all factories that are using anodizing technology both environmentally and economically.

1.2 Literature Review

An attempt has been made on the removal of sulfate anions by an ion exchange resin. Haghsheno et al. (2009) were focused on the removal of sulfate anions from the Sarcheshmeh copper complex (Kerman province, Southeast of Iran) wastewater by an anion exchange resin. The overall adsorption rate constants were compared for different initial concentrations. Lawatit K6362 resin was used to remove sulfate ion from copper mine effluents. The results show that the resin can efficiently remove sulfate anions concentration in ranges of 500–900mg/l.

Rice straw was converted into a strong basic anion exchanger by reaction with NaOH, epichlorohydrin, and trimethylamine (RS-AE). RS-AE exhibits a good sulfate adsorption performance and a higher selectivity and it can be recovered with a slight loss of adsorption capacity. NaOH treatment has a remarkable effect on the performance of exchangers; sulfate adsorbtion efficiency changes from 43.4 to 79.2% by changing the NaOH concentration between 5-30%. Also the results shows that sulfate adsorption efficiency increases from 56 to 75% by increasing quaternization temperature from 65 to 85°C(Cao et al., 2011).

Guimarães and Leão (2014) studied on sulfate removal from aqueous solutions was investigated by Amberlyst A21, a polystyrene weak base ion exchange resin. Both the pH and initial sulphate concentration were observed to strongly affect sorption

yields in the treatment of a real effluent. In all studied conditions, the maximum sulfate loading resin varied between 8 and 40 mg (SO_4^{2-}) mL (resin)$^{-1}$.

The efficiency of four solid wastes used as anion exchangers to remove chloride and sulfate ions from alkaline mining process water was investigated. The optimal adsorption parameters were estimated with synthetic solution. The maximum adsorption capacities of flotation fines (FF), filter sand (FS), pulp and paper waste (DI-60) and iron sand (RH) ranged from 221, 261, 29 and 12 mmol/g for SO_4^{2-} removal, to 106, 373, 105 and 49 mmol/g for Cl^- removal, respectively. The FF and FS removed more than 50% of both anions and RH removed approximately 80% of sulfate ions. The DI-60 removed more than 80% of both sulfate and chloride ions (Iakovleva et al., 2015).

The surface of coconut coir pith, a lignocellulosic polymer was modified with a cationic surfactant, hexadecyltrimethylammonium bromide and used as an adsorbent for the removal of sulfate from aqueous solutions. Optimum pH for maximum removal of sulfate was found to be 2.0. Equilibrium adsorption data showed good fit to Langmuir, Freundlich and D-R isotherms. Langmuir adsorption capacity was found to be 8.8 mg g^{-1}. In addition, desorption was studied to show that recovery of sulfate from the spent adsorbent was feasible (Namasivayam and Sureshkumar, 2007).

The effects of FAZ (synthesized zeolite made from fly ash) diameter, dosage and contact time on the removal SO_4^{2-} from monosodium glutamate wastewater were analyzed. It was strongly suggested that the removal ratio of SO_4^{2-} could reach 67.3% when FAZ dosage was 20 g/L, contact adsorption time was 60 minutes and adsorption temperature was room-temperature, and it was appropriate to select 100 mesh as the removal ratio and economy were comprehensively considered (Liu et al., 2010).

Bingöl (2013) focused on the adsorption of sulfate ions to the chitosan particles formed by cross-linked chitosan. A maximum sulfate removal efficiency of 32.7% was reached during initial sulfate anions concentration was 10000 mg/l. Besides, it was determined that sulfate removal percentage decreases by increasing adsorbtion temperature.

Sulfate adsorption by poly (*m*-phenylenediamine)s (PmPDs) with various oxidation states synthesized through chemically oxidative polymerization was investigated.

The rate constant is as high as 425.5 mg/(g·min) in the short equilibrium time of 30 min. The estimated highest adsorptivity of sulfate ions is 95.1% (Sang et al., 2013).

A novel method of removing sulfate from acid mining drainage (AMD) water was developed by depositing polypyrrole into the pores of wood-based activated carbon (RGC) using in situ chemical oxidative polarization. This polypyrrole-tailored activated carbon hosted positively charged polypyrrole functionality that offered sorption capacity for sulfate. Specifically, in batch tests, the polypyrrole-grafted RGC achieved a sulfate loading of 48 mg/g, this being 8 times higher than for pristine RGC. Rapid Small Scale Column Tests appraised the polypyrrole-tailored RGC for removing 773 mg/L sulfate from AMD water (Hong et al., 2014).

Silva et al. (2010) worked on a method to remove sulfate ions in an acidic medium based on co-precipitation with aluminum salts, namely $AlCl_3$ and a polyaluminum salt (PAC), followed by filtration. Co-precipitation of sulfate depends highly on the pH (which is optimal at 4.5), the mass ratio between reagents and sulfate ions (which is optimal at 7:1) and time (10 min). The best results were obtained with $AlCl_3$ at a pH of 4.5 (>80% sulfate ions removal), a 10 min. reaction time and a 7:1 $AlCl_3/SO_4^{2-}$ ratio. The results with PAC showed a lower efficiency, at around 64% for a 10:1 mass ratio.

Sulfate causes considerable problems in anaerobic digesters, related to generation of sulfides, loss of electrons (and hence methane), and contamination of gas streams. The main precipitate assessed is calcium sulfate (gypsum), though the formation of complex precipitates such as jarosite and ettringite to remove residual sulfate is also evaluated. Gypsum crystallization is an effective means for bulk removal of sulfate from highly contaminated wastewaters. Precipitation processes therefore cannot economically reduce sulfate to very low levels, and post-anaerobic sulfide removal is still required to produce high-quality biogas. However, sulfate precipitation can substantially lower the cost of sulfide removal, and will enhance methane production by reduced sulfate reduction (Tait et al., 2009).

The feasibility of sulfate removal from complex laboratory wastewaters using barium and calcium precipitation was investigated by Benatti et al. (2009). The process was applied to different wastewater cases in order to study the effect of the wastewater composition on the sulfate precipitation. At a concentration of 80 g L^{-1}, barium precipitation achieved a sulfate removal up to 61.4% while calcium precipitation

provided over 99% sulfate removal in raw and oxidized wastewaters and for both samples. Calcium precipitation was chosen to be performed after Fenton's oxidation; hence, this process configuration favors the production of higher quality precipitates. The results showed that, when dried at 105°C, the precipitate is composed of hemidrate and anhydrous calcium sulfate (w99.8%) and trace metals (w0.2%: Fe, Cr, Mn, Co, Ag, Mg, K, Na), what makes it suitable for reuse in innumerous processes.

The feasibility of sulfate removal from sulfate-rich wastewater using an anaerobic fixed bed reactor was investigated. The bioreactor was installed at a chemical industry producing organic peroxides, which generate wastewater with sulfate concentrations ranging from 12000 to 35000 mg SO_4^{2-} l^{-1}. A maximum sulfate removal efficiency of 97% was reached during discontinuous and semi-continuous operations (Silva et al., 2002).

It was reported on the application of ultrasound during the sulfate precipitation process. We show that with as little as 10 s sonication at 24 kHz, significant increases in the rate of sulfate precipitation are observed. Ultrasound caused a significant increase in the rate of SO_4^{2-} precipitation during the reaction between sulfuric acid and calcium hydroxide. The effect of sonication is dependent on the initial SO_4^{2-} concentration, with the greatest effect observed for an initial concentration of 7200 mg/L. The sulfate concentration reduces by the time during the study. At higher concentrations, the precipitation rate is still influenced by sonication, but as the non-sonicated reaction is very rapid, sonication is unlikely to be of benefit (Davies et al., 2015).

A physicochemical model for electrochemically induced reactive-transport processes is described and used for a theoretical analysis of the influence of the chemical interactions on the removal rate of the target ions. Simulations for the electro-desalination of a brick sample contaminated with a combination of these target ions are shown. Results from simulations show that the lower removal efficiency of sulfates is related to the precipitation of gypsum inside the porous body.(Paz-Garcia et al., 2013).

The effect of the chemical oxygen demand/sulfate (COD/SO_4^{2-}) ratio on the anaerobic treatment of synthetic chemical wastewater containing acetate, ethanol, and sulfate, was investigated using a UASB reactor. The experimental results show that at a COD/SO_4^{2-} ratio of 20 and a COD loading rate of 25.2 gCOD L^{-1} d^{-1}, a COD

removal of as high as 87.8% was maintained. At a COD/SO_4^{2-} ratio of 0.5 (sulfate concentration 6000 mg L^{-1}), however, the COD removal was 79.2% and the methane yield was 0.20 LCH_4/gCOD. The conversion of influent COD to methane dropped from 80.5% to 54.4% as the COD/SO_4^{2-} ratio decreased from 20 to 0.5. At all the COD/SO_4^{2-} ratios applied, over 79.4% of the total electron flow was utilized by methane-producing archaea, indicating that methane fermentation was the predominant reaction (Hu et al., 2015).

High performance thin-film composite NF membrane for the selective sulfate removal from concentrated sodium chloride aqueous with the water permeability coefficient of 75 L/(m^2 hMPa) could be prepared under specific conditions. Experimental results on concentrated mixed solution of NaCl and Na_2SO_4 demonstrated that the NF membrane developed could be successfully used for the removal of sodium sulfate from the concentrated brine of chlor-alkali industry with high permeate flux, selectivity and performance stability. The TFC NF membranes fabricated under specific conditions exhibited water permeation rate of 75 L/(m^2 h) with rejection of 65% for 2000 mg/L NaCl solution and rejection of 98% for 2000 mg/L $MgSO_4$ solution at 1.0MPa (Meihong et al., 2008).

Chemical precipitation method was investigated, which is based on formation of scarcely soluble salt by combining an anion and a cation. Metal sulfate salts are $CaSO_4$, $SrSO_4$, $PbSO_4$ and $BaSO_4$, with respect to reducing solubility. Due to the low cost and non-polluting characteristic, calcium compounds are widespread used for sulfate removal. It was determined that solid precipitate, ionic strength, presence of other ions (salting in-out effects), temperature and precipitation rate affect sulfate precipitation (Duranoğlu, 2012).

2. THEROTICAL PART

2.1 Aluminum Production and Anodic Oxidation Process

2.1.1 Aluminum profile production

Many of the very first applications of aluminum involved wrought products and the high workability of the metal in both pure and alloyed states has always been one of the greatest attractions for its use. Today, around two-thirds of aluminum produced is used in wrought forms and includes plate, sheet, extrusions, forgings, stampings, foil and wire. Extrusions are the second most common product form, and a large proportion of these are now used in the construction industry as well as the transport industry (Lamley, 2011).

The extrusion process has been likened to squeezing toothpaste out of a tube (Figure 2.1).

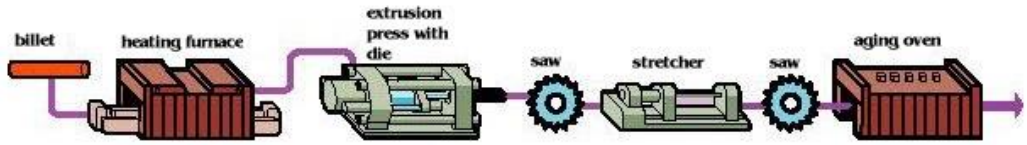

Figure 2.1 : Basic steps of aluminum profile (AEC, 2015).

When pressure is applied at the closed end, the paste is forced to flow through the open end, accepting the round shape of the opening as it emerges. If the opening is flattened, the paste will emerge as a flat ribbon. Complex shapes can be produced by complex openings. Bakers, for example, use a collection of shaped nozzles to decorate cakes with fancy bands of icing. They are producing extruded shapes (AEC, 2015).

2.1.2 Aluminum anodizing process

The surface treatment of and by metals dates back to early man using gold decoratively before 4000 BC. Gold and silver plating (including their deposit from

amalgams) were well known by the 13th century AD, and tin plating of iron was carried out in Bohemia in 1200 AD. In the mid- 19th century, the electro deposition of metals was discovered enabling new possibilities, which are still being extended.

The surface properties of metals are typically changed for:

• decoration and/or reflectivity

• improved hardness (to maintain cutting edges and resistance to damage and wear)

• prevention of corrosion.

Currently, the main areas of application are automotive and transportation, packaging, building and construction. Two further commercial areas of application have emerged since the 1960s: In microelectronics, especially with the advent of telecommunications and microprocessor controls in many common appliances. These demand mass-produced components with high conductivity capable of carrying very small electrical currents. This is achieved by applying precious metal plating on cheaper substrates in printing, where aluminum is usually the substrate of choice for lithographic plates.

The aluminum is first treated by electrochemical graining and anodic oxidation (anodizing) prior to photosensitive treatments.

Anodic oxidation (Anodizing) is known as “Eloksal” in Turkey, coming from first two letters of *el*ektrolytische *Ox*idation von *Al*uminum in German. Traditionally, the anodization of aluminum is used to protect metals from corrosion and to increase the abrasive and adsorption properties, hardness, etc. Aluminum and aluminum alloys have some inherent resistance to atmospheric corrosion due to the presence of a protective oxide film that forms immediately the metal is exposed to air. This oxide film is about 0.1-0.4x10-6 in. or 0.25-1 x 10-2 microns thick. Anodic oxidation, or anodizing, is an electrolytic process for producing very much thicker oxide coatings whose improved physical and chemical properties have greatly increased the field of application for aluminum (Stojadinovic et al., 2014; Henley, 1982).

Aluminum is normally (90 % of cases) anodized in sulfuric acid electrolyte. For special applications, aluminum may be anodized in many different types of process solution: phosphoric acid, sulfuric/oxalic acids, sulfuric/salicylic acids and chromic acid electrolytes (EC, 2006).

On most aluminum alloys a colorless, transparent aluminum oxide is formed, but alloys containing high quantities of elements such as iron, manganese, silicium and others tend to give grayish or brownish colored layers. The anodizing voltage is in the range of 17 – 22 V and the temperature of the electrolyte is generally 20 °C±5°C and electrolyte concentration is generally 190 g/l ± 40 g/l H_2SO_4. A film thickness of 5 - 30 µm is used for decorative and protective sulfuric acid anodizing. The working parameters may vary according to the application, especially in architectural anodizing. Sulfuric acid anodized coatings are often colored by special coloring processes, as shown in Figure 2.2. The oxide coating is sealed to obtain improved corrosion resistance (EC, 2006).

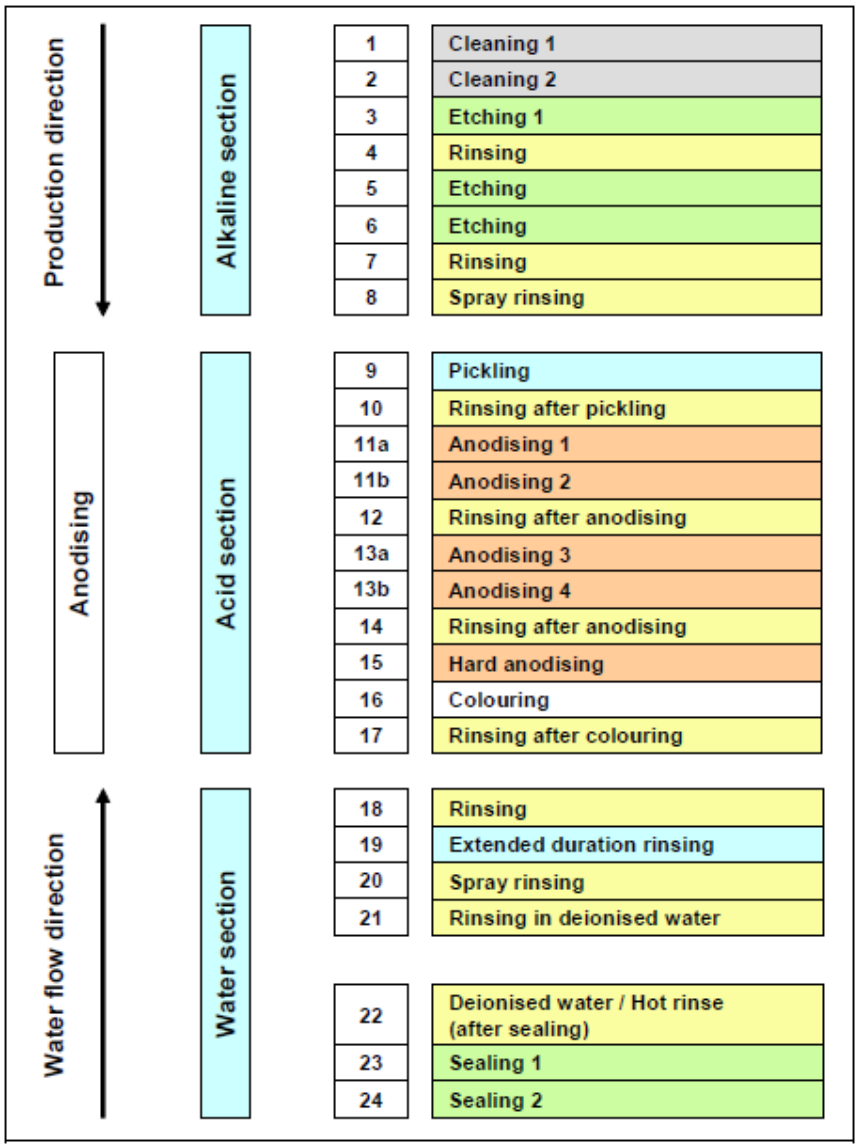

Figure 2.2 : Typical anodizing plant layout (EC, 2006).

In hard anodizing, a film thickness of 25 – 250 μm is obtained. The electrolyte is operated at - below 5 °C. Processes with oxalic acid and sulfuric acid with organic additions can also be used for hard anodizing. The hard anodizing layer is normally not sealed. In this state, it can be impregnated with lubricants (EC, 2006).

Anodizing is an electrolytic process that uses acids from the combined electrolytic solution/acid bath tank to convert the metal surface into an insoluble oxide coating. After anodizing, metal parts are typically rinsed and then sealed. Anodizing operations produce contaminated wastewaters and solid wastes (Wang et al., 2009).

When aluminum is anodically polarized in an electrolyte, negatively charged anions in the solution migrate to the anode where they are discharged with the loss of electrons. In aqueous solutions, anions usually contain oxygen, which reacts chemically with the aluminum. In reality, anodic films contain hydrated forms of the oxides. The metal oxide formation reactions may be considered to occur via the anodic dissolution of metal to form the corresponding cations:

$$Al \rightarrow Al^{3+} + 3e^{-} \quad \textbf{(2.1)}$$

followed by reaction between the metal cation and ionic oxygen:

$$2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3 \quad \textbf{(2.2)}$$

The net reaction of anodic oxidation of Al is usually given as follows:

$$2Al + 3H_2O \rightarrow A_2O_3 + 6H^{+} + 6e^{-} \quad \textbf{(2.3)}$$

The result of the anodic oxidation depends on a number of factors, particularly the electrolyte (its nature, concentration and temperature) and the conditions of electrolysis (current and voltage) (Yerokhin and Khan, 2010).

2.2 Aluminum Plant

Aluminum Plant is placed in 1st OIZ in Bilecik. The plant has production, powder coating, decorative film coating, mechanical treatments, shrink, warehouse, quality control, refinement, and recycling departments. Production process department consists of four facilities such as casthouse, extrusion press, surface treatment and

anodizing, constitutively. In casthouse, aluminum billets are produced from scrap aluminum ingots, which are some of produced in recycling plant and additives; formed as profiles by extrusion process, obtained the desired appearance according to customer requests by surface treatment and improved the resistance by anodic oxidation (anodizing). Dyeing and film coating also are applied in order to give a decorative appearance, with the exception of surface treatments. The aluminum profiles are uncolored by powder coating after pretreated in chromate pool or coated with wood, marble or granite patterns in decorative film coating department. Short cutting, angular cutting, punching, drilling and deburring processes are performed as the mechanical treatments. The tests and analyzes are carried out in quality control units and laboratories. The profiles, which are ready for sale, covered with shrink and nylon packing applications and stored in warehouse. The effluents are treated in refinement plant.

2.2.1 Production process department

The scrap aluminum ingots, which were provided from several places and produced in recycling plant are melted in the furnace and blended with appropriate amounts of Cu, Fe, Sr, Mg metals. The mixture is sent to the degassed and H_2 is removed using argon gas. The mixture leaving the degassed is filtered and billets are casted. The billets formed to aluminum profiles by extrusion process. The profiles are exposed the aging process, sent to the surface treatment process or anodized according to customer requests.

Surface treatment department has four parts including polishing, satin brushing, sandblasting and grinding. Satin brushing is applied for dulling and burring by water and steel brush. Polishing is carried out in order to polish the surface using fabric brush. In sandblasting process, it is patterned and burred by 20-µm-diameter steel balls. Grinding is a rarely applied process, which aimed to pattern.

The anodizing is the process that occurs almost all of the wastewater in the plant, with 32 baths. 14 of these baths are rinsing baths and the remaining baths are pretreatment and process baths. Degreasing is applied to remove the grease from production steps on the profile surface using $NaCO_3$. Etching baths contains Fe and used for dulling. Neutralization is the fore-step that contains H_2SO_4 in small quantities to anodizing. Anodic oxidation part consists of 5 baths, which each has

12000 A of electric current. The baths contains 18-20 % H_2SO_4. During the anodic oxidation, porous layer occurs on the aluminum surface. Nickel, tin and ferrous baths are used for coloring and have small quantities of the metals. Sealing is applied in order to closure of the pores.

2.2.2 Refinement facility

Chemical precipitation is used as the treatment method in the facility. The acidic and basic effluents are collected in the pools separately. The acidic effluent and dissolved $BaCl_2.2H_2O$ are fed into same pool and stirred. The stirred water and basic effluent are sent together for neutralization while polyelectrolyte is added. The mixture is removed to primary clarifier and kept waited. Hence, it is poured into secondary clarifier and the sludge is removed by filterpres. Approximately 10000-m^3 wastewater is treated monthly in the facility. The treated water is sent to the four sedimentation pools in order and finally sent to the treatment facility of OIZ.

2.3 Sulfate Ion Damages

Sulfate is a naturally occurring anion. High concentrations of sulfate in drinking water may cause transitory diarrhea (U.S. EPA, 1990). A study of adults found that most experienced a laxative effect above 1000 mg/L, whereas medical case reports indicate that bottle-fed infants develop diarrhea at sulfate levels above 600 mg/L. Acute diarrhea can cause dehydration, particularly in infants and young children who may already have a microbial diarrheal condition (Haghsheno et al., 2009; Cohn et al.,1999).

3. EXPERIMENTAL PART

3.1 Materials

3.1.1 Wastewater samples

The effluents used in the study were original wastewaters and provided from the anodic oxidation process units of the Factory. They were containing other compounds in them such as aluminum, nickel, tin, sodium, carbonate and hydrogen ions, additives, along with sulfate. The acidic effluents mostly contain nearly 7000 mg/L sulfate content as initial concentration. The pH values of the acidic and basic wastewaters were 1.18 and 13.50, respectively.

3.1.2 Precipitation by chemical

3.1.2.1 Decision on chemicals

In the wastewater treatment facility of the Plant, $BaCl_2.2H_2O$ is used as the precipitation chemical. Therefore, the chemicals that have similar properties with $BaCl_2.2H_2O$ were searched from the periodic table. Selected chemicals had to have two important properties. First, they should have been able to create sulfate salts in water and second they should have affordable prices in the marketplace (Table 3.1). Consequently, the $CaCl_2$ and KCl were chosen as alternative chemicals to $BaCl_2.2H_2O$. In the experiments, all the three chemicals were studied. The effectiveness of the results was made clear by comparing these chemicals. Their amounts, pH values, cost effective features and sulfate removal abilities were all compared.

Table 3.1 : Wholesale prices of chemicals used in this study.

	$BaCl_2.2H_2O$	**$CaCl_2$**	**KCl**
Price ($/kg)	0.8	0.2	1

3.1.2.2 Decision on chemical amounts

0.1 g $BaCl_2.2H_2O$ is used for 1 L of acidic effluent provided from the wastewater treatment facility of the Plant. The same amount was studied as the reference value in the experiments. It was tested with the quantities reducing by 10%, from 0.1 to 0.04 g for 1 L of sample.

3.1.3 Equipment and reagents

All chemicals utilized in this study were analytical reagent grade or better unless noted. Water was glass distilled for all solutions. Barium chloride dehydrate, Potassium Chloride and Calcium Chloride were used in the experiments for the precipitation. A commercial polyelectrolyte was used as a flocculent, alike the one used in the treatment facility of the plant. An analytical, sensitive scale (Ohaus) was used for the weight measurements. A commercial polyelectolyte that obtained from refinement facility of the Aluminium Plant was used as the flocculent.

All absorbance experiments were performed with a Jenway 7315 UV/VIS spectrophotometer. The measurements were made using Hellma 10 mm quartz cells. 2-Propanol (J.T. Baker), Glycerol (30 Bé, 99.50%, A.D.R. Group), Hydrochloric acid (37% extra pure, Riedel-de Haën) and Ultrasonic Bath (J.P. Selecta) were used to prepare conditioning reagent and Magnetic stirrer (Fisher Scientific) for UV measurements. Micropipetting was done using the Brand Transferpette automatic pipette.

Armfield Jar Test was used with four stirrers. A Mattler Toledo pH meter was used with two electrodes.

3.2 Methodology

Batch jar tests were performed in 1000 ml beakers using a total volume of 650 ml for each test at room temperature (Figure 3.1). 250 ml acidic effluent samples were first poured into the beakers. The chemicals ($BaCl_2.2H_2O$, $CaCl_2$ and KCl) were dissolved in 250 ml distilled water each in erlenmeyers and then added to the beakers. The samples were then stirred using magnetic stirrers at constant rate and the pH values were measured every 20 minutes. After 2 hours, 150 ml of basic effluents were

poured into the samples for neutralization and stirred for 15 minutes. The basic effluent volume was determined based on the pH limitations according to the Water Pollution Control Regulations for Turkey. The samples were then poured into the glass containers and left for the sedimentation throughout a day.

In the experiments with the flocculent use, the effluent that was processed with the basic effluent was used. The polyelectrolyte, which was preliminary dissolved in distilled water, was added into this solution and the resulting mixture was stirred for the next 15 minutes. At the end of the time, the mixture was poured into the glass containers and left for sedimentation for 3 hours. 0.0016, 0.0019 and 0.0022 mg were chosen as the trial amounts.

In the experiments with only basic effluent use, the acidic water itself was used. The basic effluent was added into the 250 ml of acidic water with varying volumes and it was kept stirred for 2 hours. After the stirring stage, the mixture was poured into the glass containers and left for the sedimentation for one day. 200, 400, 600 and 800 ml of volumes were chosen for the trials.

After settling was completed, the sulfate remaining in the solution was determined using UV absorbance at a wavelength of 420 nm (D516-11, 2011). An aliquot of approximately 3 milliliters of test solution was carefully removed from just below the surface for the absorbance measurement and placed in a 10 mm quartz bathtub. The measurement was made against a reference bathtub containing 3 milliliters of distilled water.

Excellent correlations were found between UV and sulfate concentration. The predictive equation produced from a linear least squares regression analysis was

Sulfate (mg/l) = 0.0327 (Absorbance) – 0.0464

Figure 3.1 : Experimental steps.

Eight calibration samples were used to develop the equation and an R^2 (correlation coefficient) value of 0.9956 was determined.

UV standards were prepared by diluting with water 0.0, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0 and 50.0 mL of 100 mg/L sample wastewater to 100-mL volumes in volumetric flasks and drawn a calibration curve showing sulfate ion content in milligrams per liter plotted against the corresponding photometer readings. These solutions have sulfate ion concentrations of 0.0, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0 and 50.0 (ppm), respectively.

0.5 mL of the treated wastewater sample was measured, diluted to 50.0 mL, added 2.5 ml of conditioning reagent and mixed by magnetic stirrer. While the solution was being stirred, 0.15 g of $BaCl_2.2H_2O$ crystals was added and timing has been started immediately. The mixture was stirred exactly 1.0 minute at constant speed. Immediately after the stirring period has ended, the solution was poured into the cell and was measured at 420 nm against distilled water as the blank.

4. RESULTS AND DISCUSSION

In this study, the treatability of the effluent highly loaded with the sulfate ions was studied by using the chemical precipitation method. Batch jar test sets were used for the experiments and sulfate ions were precipitated as sulfate salts. Optimum chemical amount and chemical type were determined. The results of the study were presented in this section.

4.1 Precipitation with $BaCl_2.2H_2O$

Process water was being prepared by using 18-20% of H_2SO_4 in the factory. Thus, the acidic effluents obtained from the baths were containing high sulfate ion concentrations.

$$H_2SO_{4(aq)} \rightarrow H^+_{(aq)} + HSO^-_{4(aq)} \quad \textbf{(4.1)}$$

$$HSO^-_{4\,(aq)} \rightarrow H^+_{(aq)} + SO_4^{2-}{}_{(aq)} \quad \textbf{(4.2)}$$

The chemical of $BaCl_2.2H_2O$, preliminary dissolved in water, was added to the effluent and $BaSO_4$ was formed according to the following chemical equations.

$$BaCl_2.2H_2O_{(s)} \rightarrow Ba^{2+}_{(aq)} + 2Cl^-_{(aq)} + 2H_2O_{(l)} \quad \textbf{(4.3)}$$

$$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)} \quad \textbf{(4.4)}$$

The sulfate concentration in the solution was decreased by $BaSO_4$ formation. H^+ ions were combined with Cl^- ions and formed HCl acid. Since HCl acid is a strong acid, it was ionized repeatedly and the pH value was under the limit value. Basic effluents were added to the mixture for neutralization purpose. Due to its high concentration of NaOH which was later ionized to Na^+ and OH^- ions, the ions formed NaCl and H_2O together with the H^+ and Cl^- ions.

$$NaOH_{(s)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)} \quad \textbf{(4.5)}$$

$$Na^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow NaCl_{(aq)} \quad \textbf{(4.6)}$$

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(l)} \quad \textbf{(4.7)}$$

The sulfate concentrations after the treatment and sulfate removal percentages were given in Table 4.1 as the results of the study of treatment with $BaCl_2.2H_2O$.

Table 4.1 : Sulfate concentration and sulfate removal percentage of treated water.

Amount of chemical used (g/L)	Sulfate concentration after treatment (mg/L)	Sulfate removal (%)
0.1	1241.28	82
0.09	1264.22	82
0.08	1270.34	82
0.07	1253.52	82
0.06	1357.49	81
0.05	1340.67	81
0.04	1377.37	80
0.03	1340.67	81

The pH values measured during the stirring period for each 20 minutes and the final pH values measured after the settling period which was 24 hours were given in Table 4.2.

Table 4.2 : pH value of the effluent during the treatment.

	Amount of chemical (g/L) / pH							
Time	**0.1**	**0.09**	**0.08**	**0.07**	**0.06**	**0.05**	**0.04**	**0.03**
0 min	1.35	1.38	1.41	1.48	1.42	1.42	1.51	1.52
20 min	1.38	1.42	1.47	1.45	1.4	1.39	1.46	1.5
40 min	1.44	1.42	1.46	1.44	1.38	1.38	1.47	1.47
60 min	1.36	1.41	1.42	1.45	1.38	1.39	1.47	1.47
80 min	1.38	1.41	1.43	1.42	1.38	1.38	1.42	1.43
100 min	1.40	1.43	1.45	1.43	1.36	1.37	1.44	1.44
120 min	1.35	1.40	1.42	1.40	137	1.37	1.37	1.40
24 hours	**9.42**	**9.42**	**10.78**	**9.30**	**9.40**	**10.71**	**9.94**	**9.23**

The concentrations of sulfate ions changed according to the chemical amounts added (Figure 4.1). The maximum and minimum values were 1377.37 mg/L and 1241.28 mg/L obtained from the treatment with 0.04 and 0.1 g/L of chemical use, respectively. All the amounts tried can be used for the treatment, because all results were under the limit value.

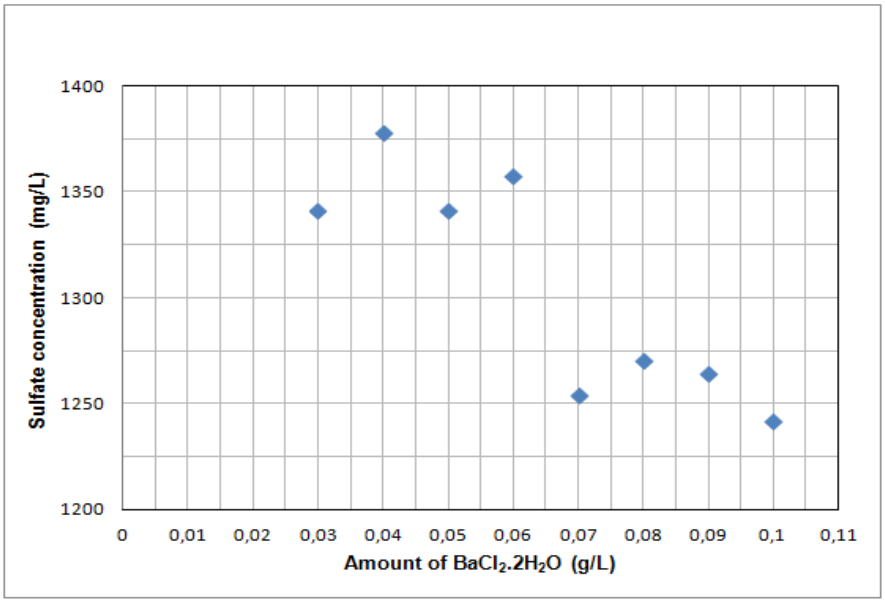

Figure 4.1 : Sulfate concentration of water after treatment with $BaCl_2.H_2O$.

Figure 4.2 shows the sulfate removal percentages ranged in 80-82%. The percentage decreased by nearly 1% when the value of the chemical used was changed from 0.07 g/L to 0.06 g/L. After this circumstance, the results tied close to each other.

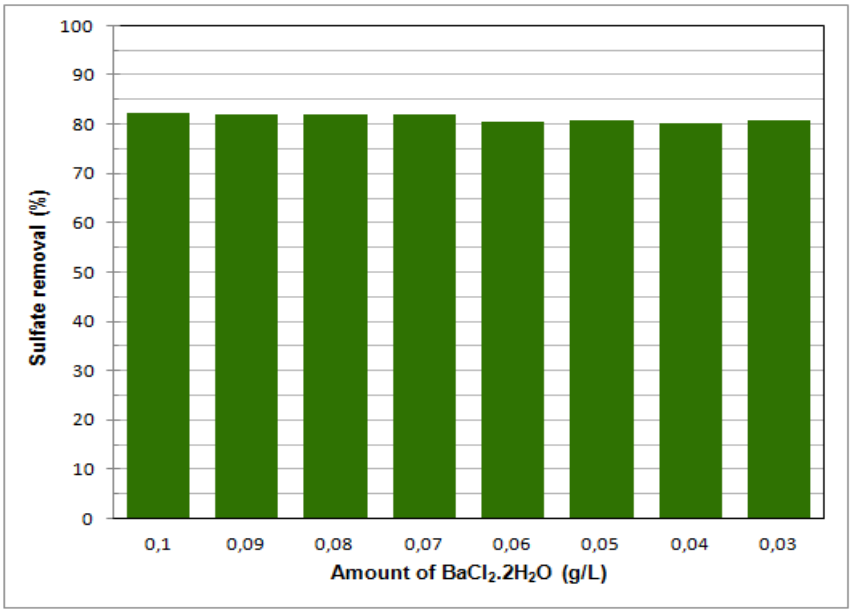

Figure 4.2 : Sulfate removal percentage after treatment with $BaCl_2.2H_2O$.

The pH values were almost unchanged during the treatment as shown in Figure 4.3. Therefore, the stirring was ended after 2 hours. It was determined that the chemical amounts used did not really affect the pH values, which were in between 1.35 and 1.40 after 2 hours. The final pH values were approximately under the limit value (Figure 4.4).

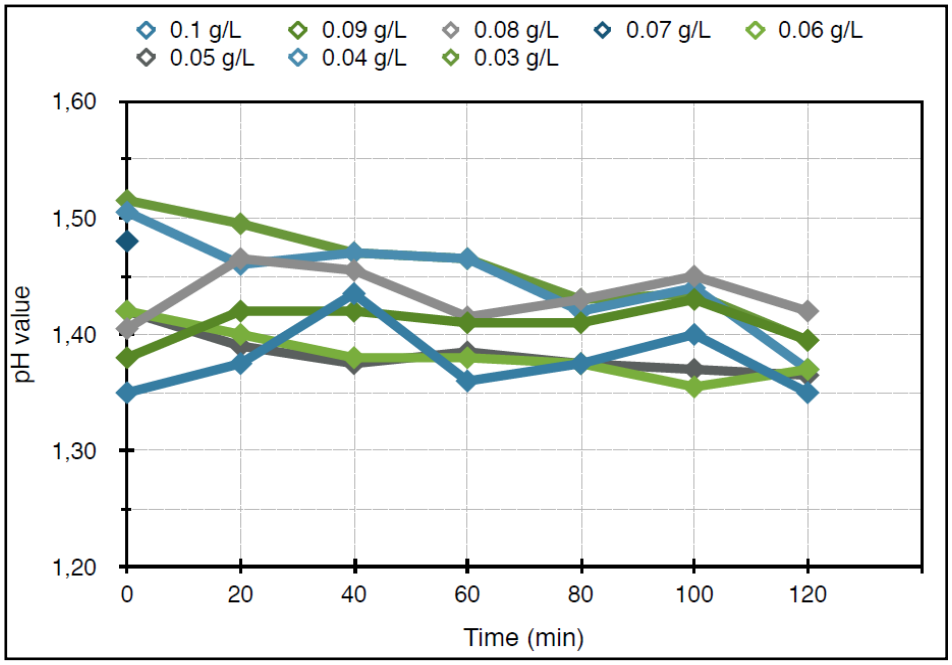

Figure 4.3 : pH values measured during the treatment with $BaCl_2.2H_2O$.

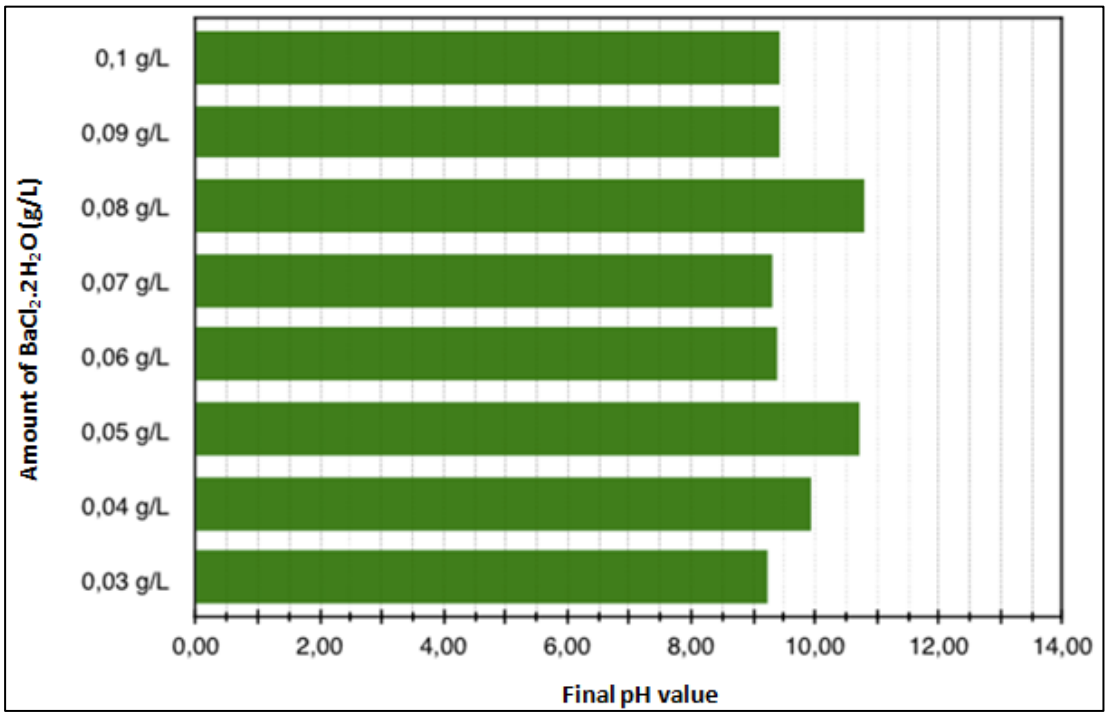

Figure 4.4 : Final pH values after settling for $BaCl_2.2H_2O$.

4.2 Precipitation with $CaCl_2$

The acidic effluent contains high SO_4^{2-} ions because of using 18-20% H_2SO_4 in anodising process. H_2SO_4 was ionized according to the Equations 4.1 and 4.2.

The chemical of $CaCl_2$, preliminarily dissolved in water was added to the effluent and $CaSO_4$ were formed according to the following chemical equations.

$$CaCl_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \quad \textbf{(4.8)}$$

$$Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow CaSO_{4(s)} \quad \textbf{(4.9)}$$

The sulfate concentration was decreased by $CaSO_4$ formation. H^+ ions were combined with Cl^- ions and formed HCl acid. Since HCl acid is a strong acid, it was ionized repeatedly and pH value was under the limit value. Basic effluents were added to the mixture for neutralization purpose. Due to its high concentration of NaOH which was later ionized to Na^+ and OH^- ions, the ions formed NaCl and H_2O together with H^+ and Cl^- ions, according to Equations 4.5, 4.6 and 4.7

The sulfate concentrations after the treatment and sulfate removal percentages were given in Table 4.3 as the results of the study of treatment with $CaCl_2$.

Table 4.3 : Sulfate concentrations and sulfate removal percentages of treated water.

Amount of chemical used (g/L)	Sulfate concentration after treatment (mg/L)	Sulfate removal (%)
0.1	1303.98	81
0.09	1326.91	81
0.08	1343.73	81
0.07	1427.83	80
0.06	1374.31	80
0.05	1326.91	81
0.04	1308.56	81
0.03	1371.25	80

The pH values measured during stirring period for each 20 minutes and the final pH values measured after the settling period which was 24 hours were given in Table 4.4.

Table 4.4 : pH value of the effluent during the treatment.

	Amount of chemical (g/L) / pH							
Time	**0.1**	**0.09**	**0.08**	**0.07**	**0.06**	**0.05**	**0.04**	**0.03**
0 min	1.32	1.34	1.37	1.34	1.34	1.33	1.28	1.28
20 min	1.33	1.32	1.28	1.27	1.31	1.33	1.24	1.23
40 min	1.31	1.33	1.30	1.27	1.33	1.34	1.26	1.25
60 min	1.35	1.31	1.32	1.28	1.28	1.31	1.27	1.29
80 min	1.31	1.31	1.28	1.26	1.30	1.25	1.32	1.29
100 min	1.27	1.28	1.25	1.25	1.29	1.28	1.29	1.30
120 min	1.26	1.25	1.28	1.31	1.29	1.29	1.27	1.26
24 hours	**9.21**	**9.27**	**9.63**	**9.89**	**9.68**	**10.17**	**9.42**	**9.65**

The concentrations of sulfate ions changed according to the chemical amounts added (Figure 4.5). The minimum and maximum values were 1303.98 mg/L and 1427.83 mg/L obtained from the treatment with 0.1 and 0.07 g/L of chemical use, respectively. All the amounts tried can be used for the treatment, because all results were under the limit value.

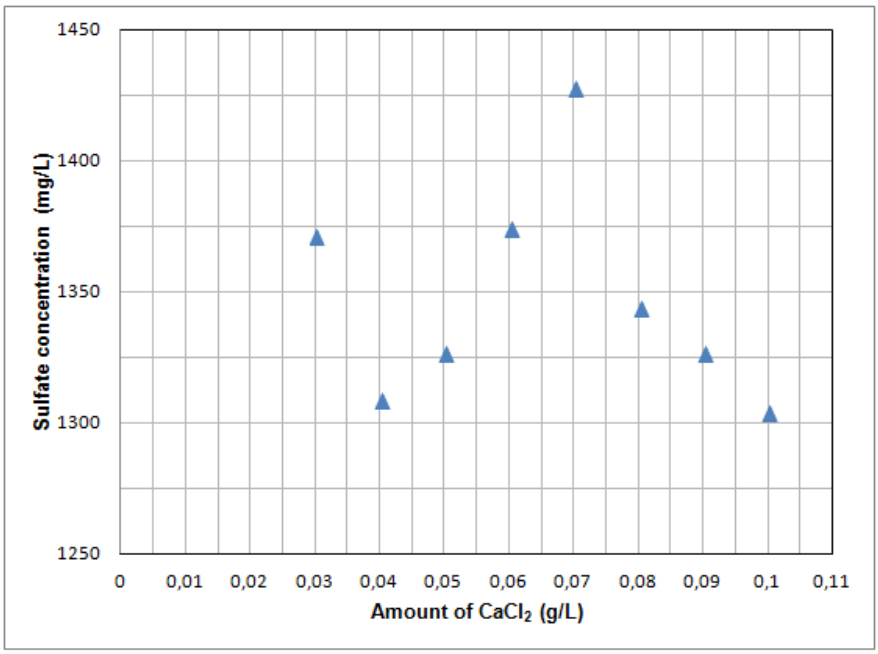

Figure 4.5 : Sulfate concentration of water after treatment with $CaCl_2$.

Figure 4.6 shows the sulfate removal percentages ranged in 80-81%. The percentages obtained have hardly changed, however there was a decrease from 0.1 g/L to 0.07 g/L and an increase from 0.06 g/L to 0.04 g/L.

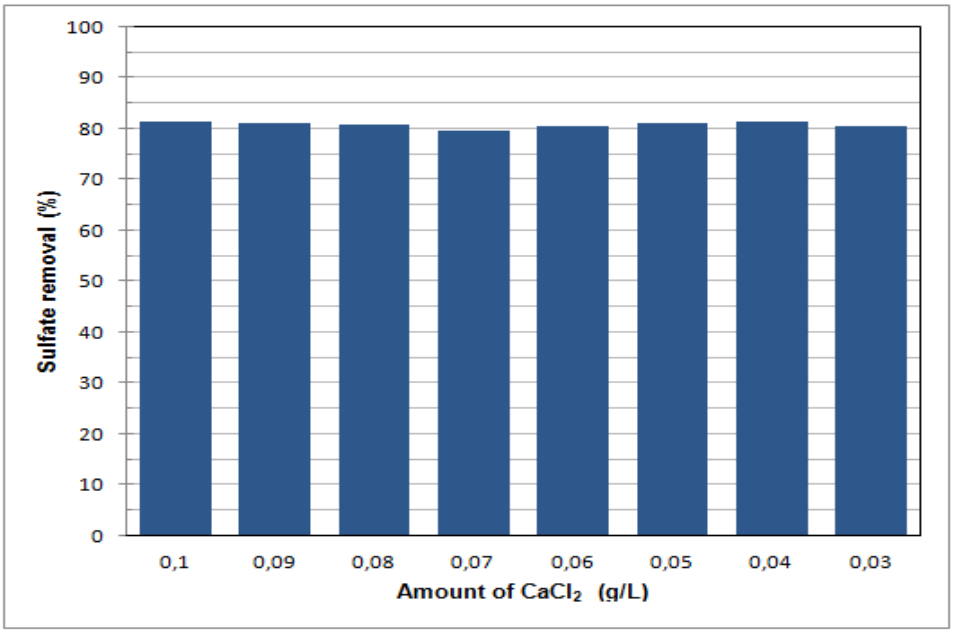

Figure 4.6 : Sulfate removal percentages after treatment with $CaCl_2$.

The pH values were almost unchanged during the treatment as shown in Figure 4.7. Therefore, the stirring was ended after 2 hours. It was determined that the chemical amounts used did not really affect the pH values which were in between 1.26 and 1.31 after 2 hours. The final pH values were approximately under the limit value. The final results were around 10 as shown in Figure 4.8, the maximum limit, because maximum quantity of basic effluent that provides the maximum limit has chosen and added for neutralization.

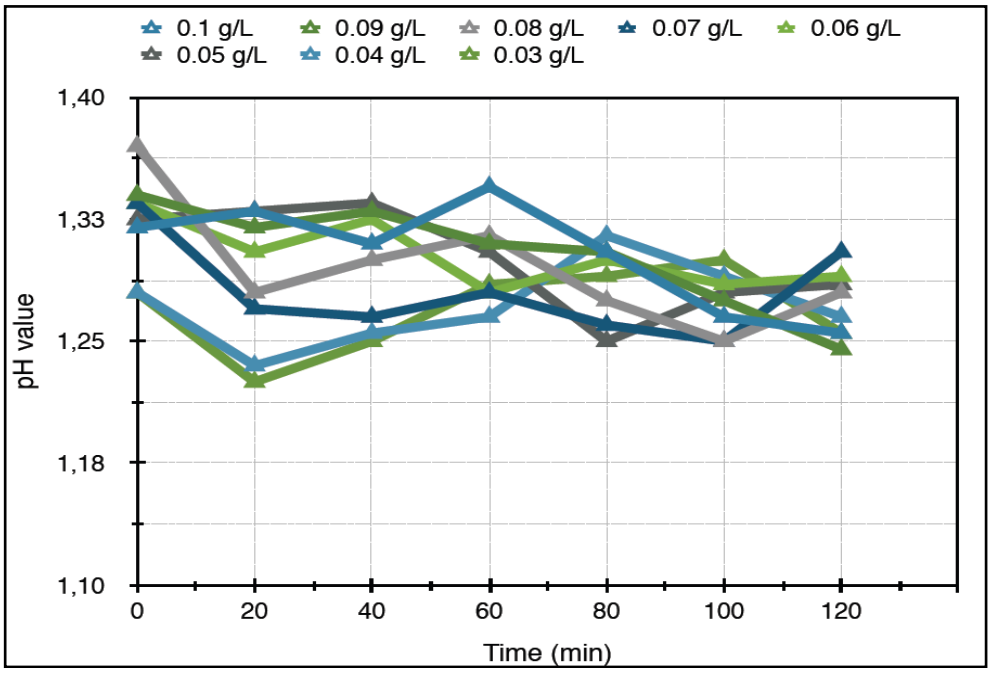

Figure 4.7 : pH values measured during the treatment with $CaCl_2$.

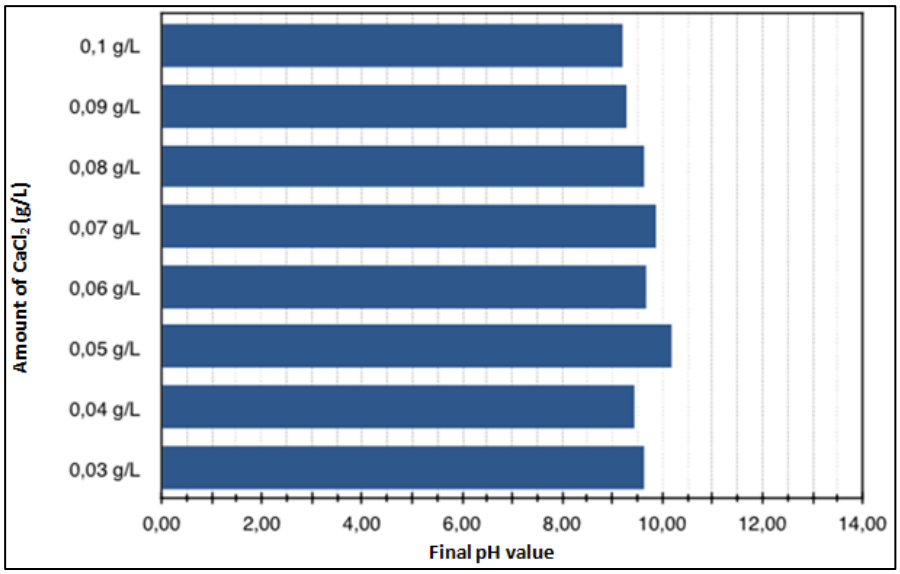

Figure 4.8 : Final pH values after settling for $CaCl_2$.

4.3 Precipitation with KCl

High concentration of sulfuric acid is used in the anodising process baths hence the acidic effluent has high sulfate concentration. H_2SO_4 ionization was given in Equations 4.1 and 4.2.

KCl was dissolved in water and added to the effluent. The effluent was containing small quantities of aluminum ions due to the nature of the anodizing process. Potassium, aluminum and sulfate ions were all associated with water molecules and formed $KAl_3(SO_4)_2(OH)_6$ which is known as "alunite".

$$KCl_{(s)} \rightarrow K^+_{(aq)} + Cl^-_{(aq)} \quad \textbf{(4.10)}$$

$$3Al^{3+}_{(aq)} + K^+_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 6H_2O_{(l)} \leftrightarrow KAl_3(SO_4)_2(OH)_{6(s)} + 6H^+_{(aq)} \quad \textbf{(4.11)}$$

The sulfate concentration was decreased by $KAl_3(SO_4)_2(OH)_6$ formation. H^+ ions were combined with Cl^- ions and formed HCl acid. Since HCl acid is a strong acid, it was ionized repeatedly and the pH value was under the limit value. Basic effluents were added to the mixture for neutralization purpose. Due to its high concentration of NaOH which was then ionized to Na^+ and OH^- ions, the ions formed NaCl and H_2O together with H^+ and Cl^- ions, according to the Equations 4.5, 4.6 and 4.7

The sulfate concentrations and sulfate removal percentages were given in Table 4.5 as the results of the study of treatment with KCl.

Table 4.5 : Sulfate concentrations and sulfate removal percentages of treated water.

Amount of chemical used (g/L)	Sulfate concentration after treatment (mg/L)	Sulfate removal (%)
0.1	1305.50	81
0.09	1334.56	81
0.08	1380.43	80
0.07	1441.59	79
0.06	1374.31	80
0.05	1362.08	81
0.04	1398.78	80
0.03	1372.78	80

The pH values measured during stirring period for each 20 minutes and the final pH values measured after the settling period which was 24 hours were given in Table 4.6.

Table 4.6 : pH value of the effluent during the treatment.

	Amount of chemical (g/L) / pH							
Time	**0.1**	**0.09**	**0.08**	**0.07**	**0.06**	**0.05**	**0.04**	**0.03**
0 min	1.29	1.26	1.38	1.34	1.31	1.24	1.22	1.22
20 min	1.33	1.34	1.37	1.37	1.34	1.35	1.21	1.22
40 min	1.34	1.33	1.35	1.35	1.34	1.35	1.26	1.28
60 min	1.32	1.29	1.36	1.36	1.35	1.35	1.30	1.29
80 min	1.29	1.29	1.35	1.33	1.34	1.38	1.27	1.31
100 min	1.31	1.31	1.31	1.32	1.34	1.35	1.27	1.30
120 min	1.31	1.30	1.31	1.29	1.35	1.33	1.33	1.32
24 hours	**9.80**	**9.26**	**10.15**	**9.33**	**9.76**	**9.71**	**9.23**	**9.36**

The concentrations of sulfate ions changed according to the chemical amounts added (Figure 4.9). The maximum and minimum values were 1441.59 mg/L and 1305.50 mg/L obtained from the treatment with 0.07 g/L and 0.1 g/L of chemical use, respectively. All the amounts tried can be used for the treatment, because all results were under the limit value.

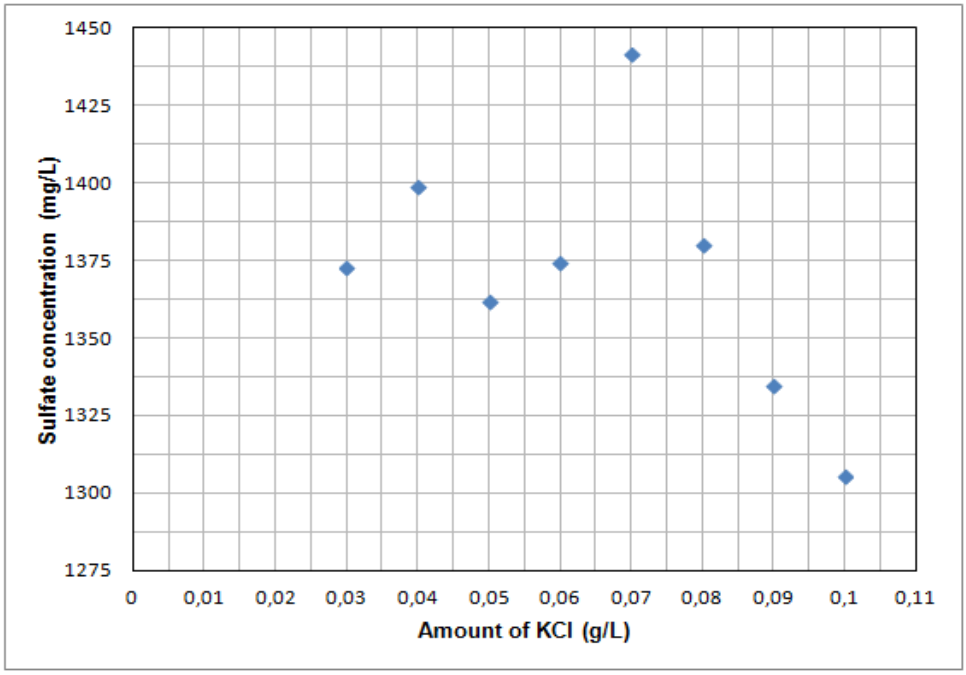

Figure 4.9 : Sulfate concentration of water after treatment with KCl.

Figure 4.10 shows the sulfate removal percentages ranged in 79-81%. The percentage has decreased sharply from 0.1 g/L to 0.07 g/L. Then it had tendency to move upward to 81%.

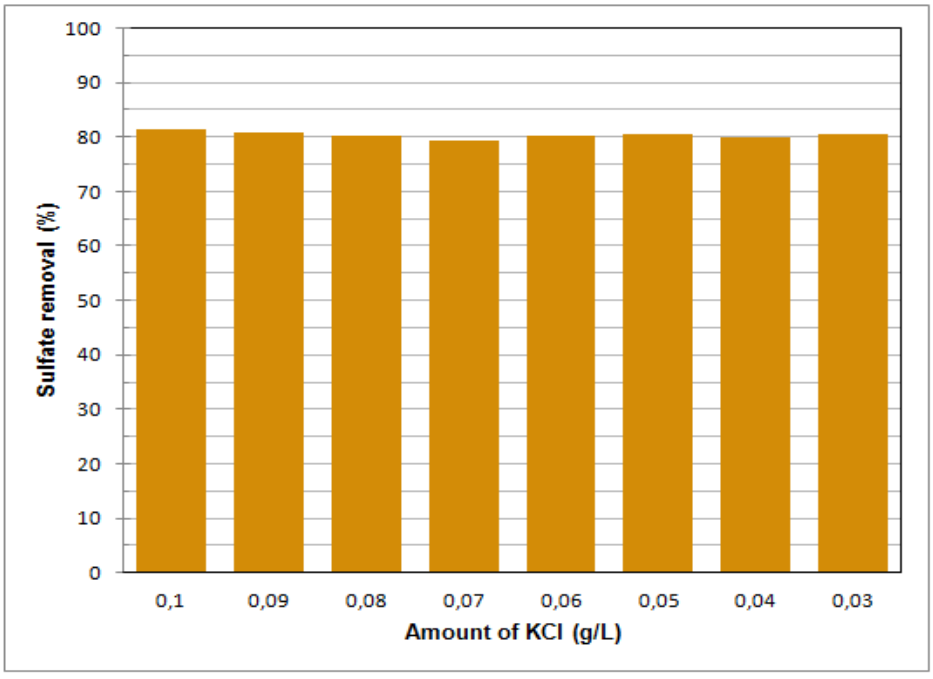

Figure 4.10 : Sulfate removal percentage after treatment with KCl.

The pH values were almost unchanged during the treatment as shown in Figure 4.11. Therefore, the stirring was ended after 2 hours. It was determined that the chemical

amounts used did not really affect the pH values, which were in between 1.29 and 1.35 after 2 hours. Figure 4.12 shows the pH values after treatment with KCl. The results are in the range of the limitation.

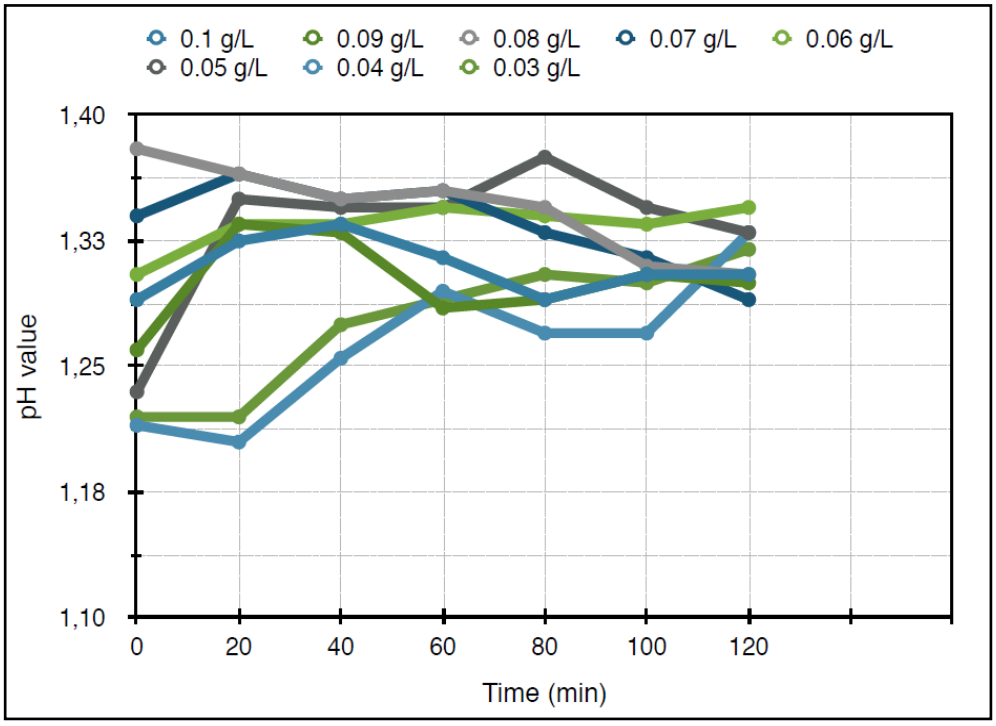

Figure 4.11 : pH values measured during the treatment with KCl.

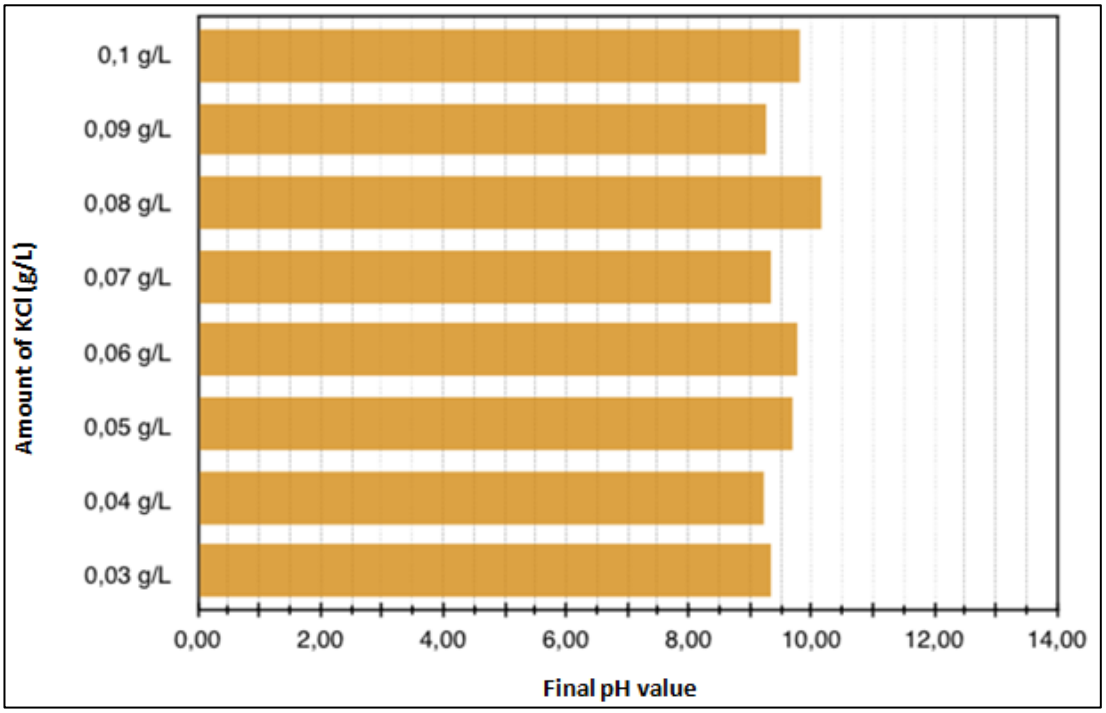

Figure 4.12 : Final pH values after settling.

4.4 Comparison of the Compounds

Figure 4.13 shows that all the chemicals were successful in removing the sulfate ions from the effluent. The percentages changed in between 79 and 82 generally and the individual ranges were 80-82% for $BaCl_2.2H_2O$, 80-81% for $CaCl_2$ and 79-81% for KCl, separately. By comparison, the effectiveness of the chemicals can be ordered as $BaCl_2.2H_2O$>$CaCl_2$>KCl. The maximum and minimum sulfate removal percentages belonged to $BaCl_2.2H_2O$ and KCl, with 0.1 and 0.07 g per 1 L of effluent. There is no linear relation between the chemical amounts and sulfate removal quantities, but it can be said that amounts between 0.08 and 0.1 g/L were more effective than the other quantities.

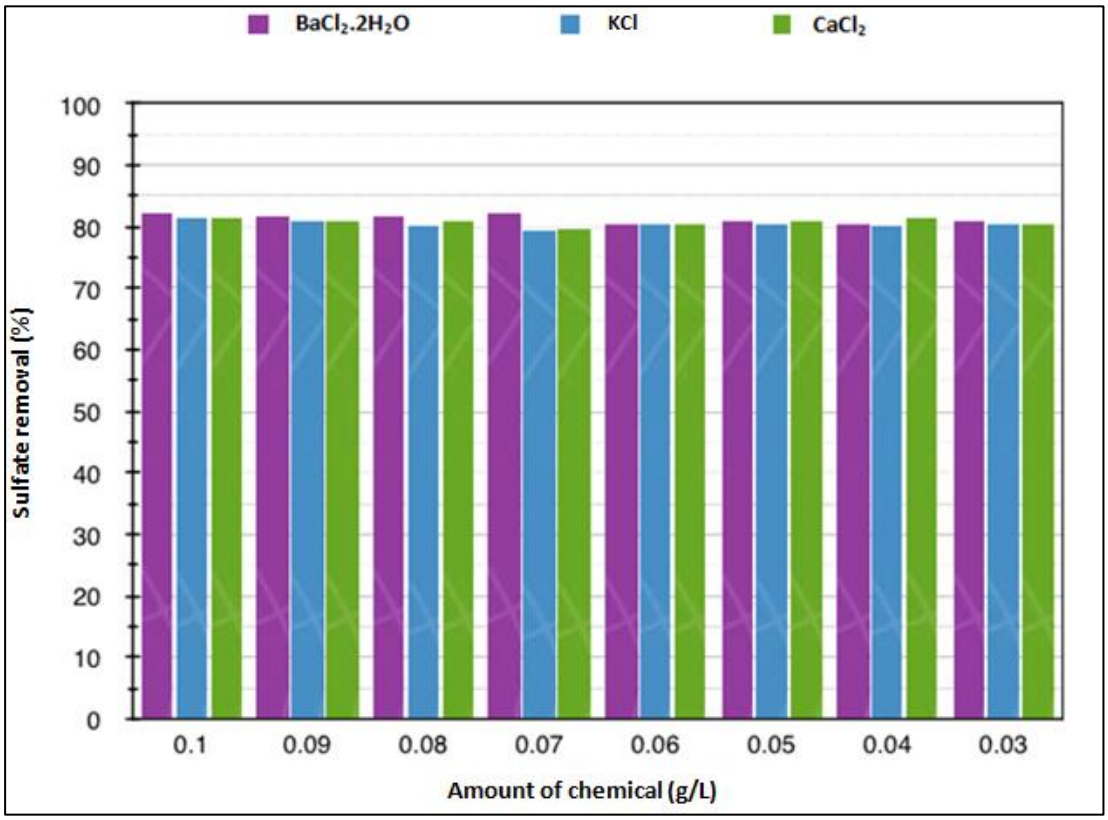

Figure 4.13 : Sulfate removal percentages after treatment.

The pH values obtained ensured the Turkish discharging limit value that is 10. Almost all pH values remained low from this limit as shown in Figure 4.14. Four pH values only were identified above 10, and the residue of 0.15-0.78 can be neglected.

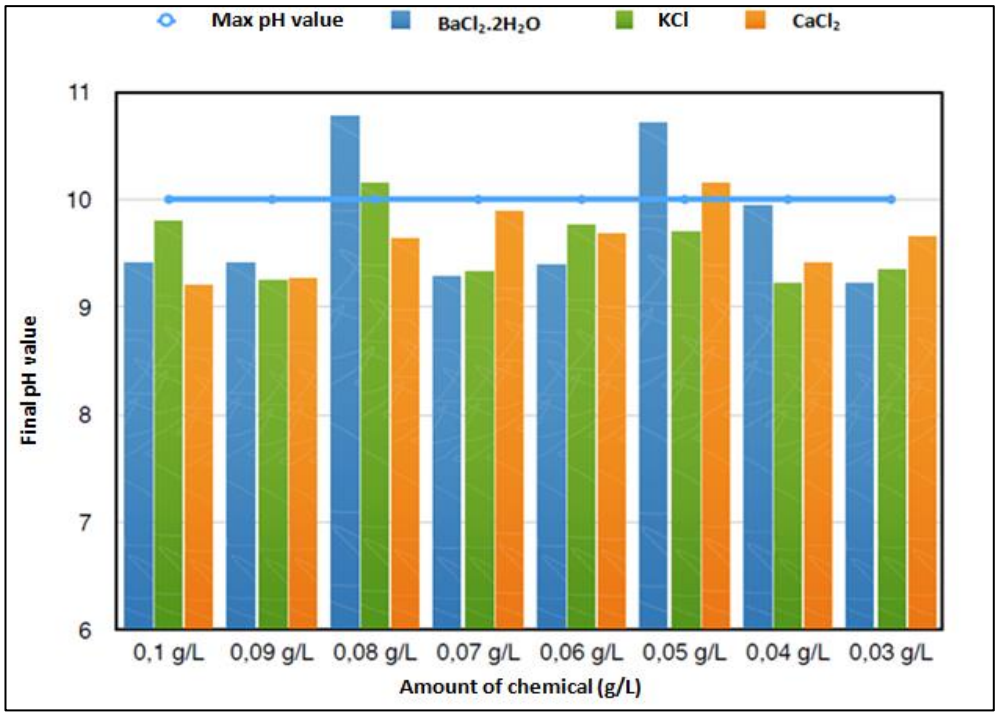

Figure 4.14 : Final pH values for treated water.

4.5 Effect of Flocculent

To determine the effect of the flocculent, experiments were performed by using 0.05 g/l of each chemical. Three different quantities of polyelectrolyte were used and the results were compared with each other and no-use trial. As shown in Figures 4.15 and 4.16, polyelectrolyte use affected the treatment positively.

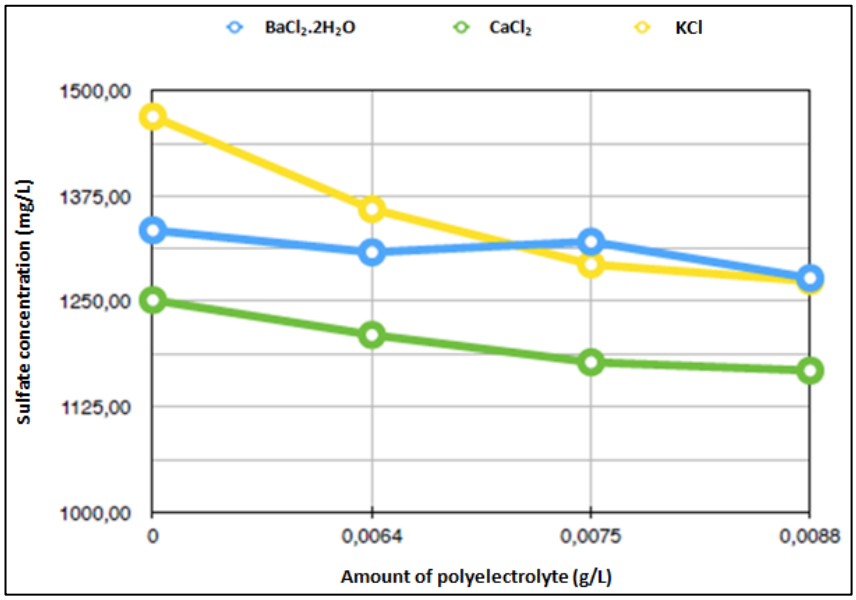

Figure 4.15 : Sulfate concentration of water after treatment with chemical and flocculent.

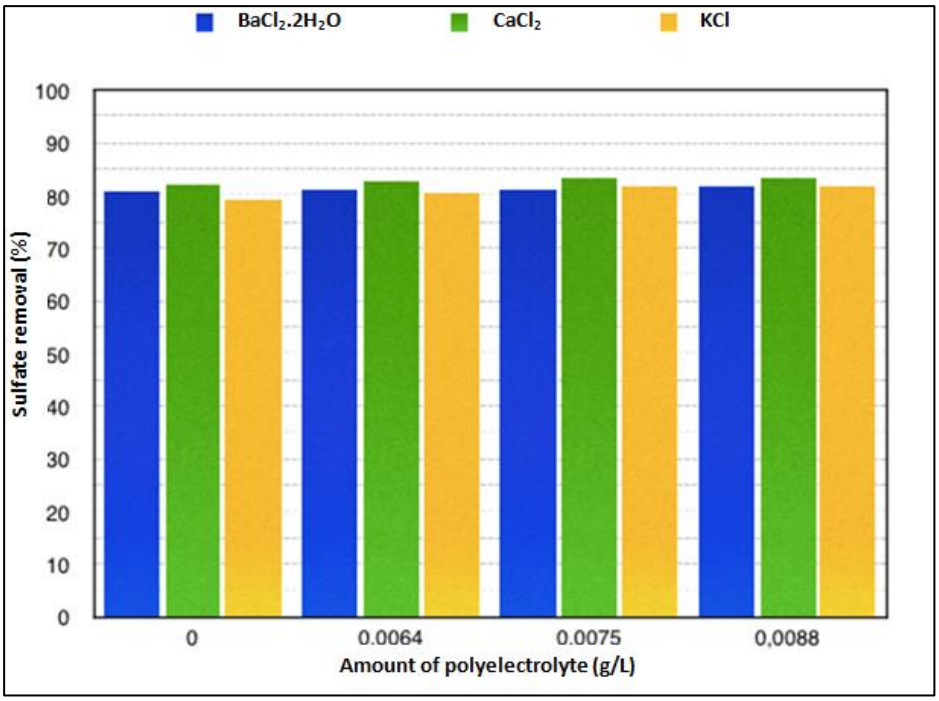

Figure 4.16 : Sulfate removal percentages after treatment using flocculent.

4.6 Neutralization Results

For all experiments, the neutralization was applied in an effort to reach the pH limitation after the precipitation. In order to determine the effect of the basic effluent on formation of the sulfate salts, an experiment with no chemical addition was also carried out and the results are shown in Figures 4.17 and 4.18.

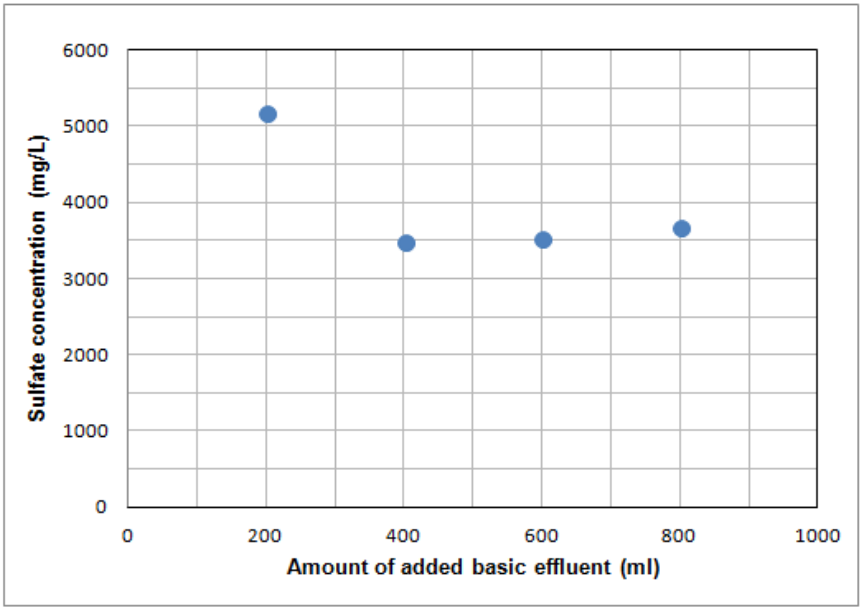

Figure 4.17 : Sulfate concentration of water treated with basic effluent.

Basic effluent addition removed almost 50% of sulfate ions. These results showed that sulfate ions in the water reacted with the aluminum and sodium ions of the basic effluent according to the Equations 4.12 and 4.13.

$$Na^{+} + Al^{3+} + 2SO_4^{2-} + 12H_2O \rightarrow NaAl(SO_4)_2.12H_2O \quad \textbf{(4.12)}$$

$$2Al^{3+} + 3SO_4^{2-} + 6H_2O \rightarrow Al_2(SO_4)_3.6H_2O \quad \textbf{(4.13)}$$

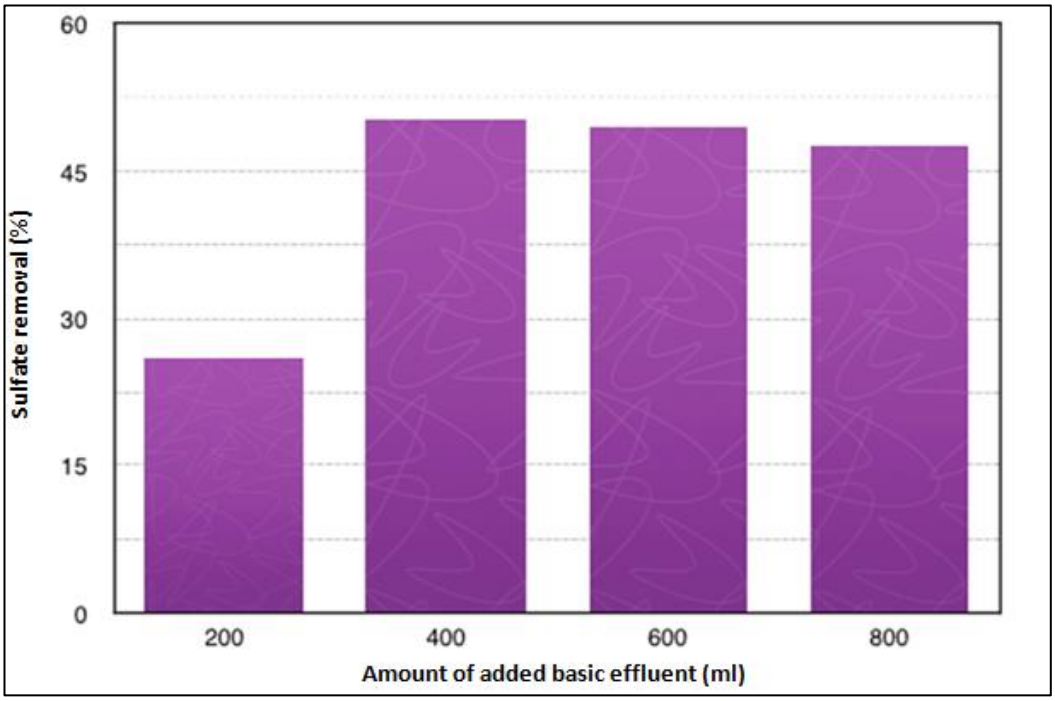

Figure 4.18 : Sulfate removal percentages after treatment with basic effluent.

5. CONCLUSIONS

The conclusions extracted from the study can be summarized as follows:

Minimum sulfate concentrations were obtained when 0.1 g of chemical was used per 1 L of acidic effluent for all three chemicals.

The minimum and maximum sulfate concentrations are 1241.28 mg/L and 1340.67 mg/L when 0.1 g and 0.04 g of $BaCl_2.2H_2O$ per 1 L of effluent are used for the precipitation, respectively. The amount of 0.1 g/L of chemical provides minimum sulfate concentration in the water. In other words, it also ensures maximum sulfate removal of 82%. Since the minimum removal percentage of sulfate is 80% for the amount of 0.04 g/L, the removal percentage of sulfate ranges in 80-82% for $BaCl_2.2H_2O$.

The minimum sulfate concentration of the water treated with 0.1 g/L $CaCl_2$ is 1303.98 mg/L with 81% of sulfate removal. Besides, the maximum sulfate concentration and the minimum sulfate removal percentage are 1427.83 mg/L and 80%, respectively when 0.07 g/L of $CaCl_2$ is used. The sulfate removal ability of $CaCl_2$ varies in 80-81%.

The minimum and maximum sulfate concentrations remained in the water are 1305.50 mg/L and 1441.59 mg/L when 0.1 g/L and 0.07 g/L KCl are used for the precipitation, respectively. The amount of 0.1 g/L of chemical provides minimum sulfate concentration in the water. In other words, it also ensures maximum sulfate removal of 81%. Since the minimum removal percentage of sulfate is 79% for the amount of 0.07 g/L, the removal percentage of sulfate is ranged as 79-81% for KCl.

Polyelectrolyte usage affects the sulfate removal positively. The most affected chemical is KCL by comparison. The removal percentage of sulfate increases from 79 to 82% by increasing the polyelectrolyte amount used. However, the affect of flocculent use on the treatment of sulfate removal with $BaCl_2.2H_2O$ and $CaCl_2$ is almost negligible. It increases the removal percentage by only 1% and keeps it

constant later on. Therefore, if $BaCl_2.2H_2O$ or $CaCl_2$ is selected as the precipitation agent, there is no need to use polyelectrolyte.

In the wastewater treatment facility of the plant, 0.1 g $BaCl_2.2H_2O$ and 0.0075 g of polyelectrolyte per 1 L of effluent are used. Since approximately 20 000 m^3 of wastewater is treated every month, 1000 kg of $BaCl_2.2H_2O$ ($0.8/kg) and 150 kg of polyelectrolyte ($6/kg) are used in the facility on the monthly basis. Therefore, the current cost spent for the chemicals is $1600+$900=$2500.

If the best results (except 0.1 g/L) which are 0.07 g/L for $BaCl_2.2H_2O$, 0.04 g/L for $CaCl_2$ ($0.2/kg) and 0.09 g/L for KCl ($1/kg) are considered, the total costs would be $1120, $160 and $1800, respectively. If the 0.03 kg/L which is minimum amount is used for all chemicals, the costs would be $480, $120 and $600 for $BaCl_2.2H_2O$, $CaCl_2$ and KCl, respectively. Accordingly, saving 81%, 95% and 76% of the chemical costs is possible.

Consequently, all three chemicals can be used for the treatment of sulfate removal with all amounts that have been experimented. They all reach the final sulfate concentrations that meet the legal limitation. The 0.03 g/L of $CaCl_2$ use might be a logical selection for a company since the optimum conditions, efficiency and cost effectiveness concerns are collectively met. Next to this, the sludge produced after the treatment will be less in scale since the $CaCl_2$ is the cheapest chemical amid all other three chemicals by comparison. For sure, this will also affect the economic gains of the company positively.

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